Supporting Information

Detailed Experiments

***Materials*:** All the reagents were analytical grate and used without further purification.

Synthesis of the Steep Rhombohedra $MnCO_3$: In a typical synthesis, 0.1 mmol of potassium permanganate ($KMnO_4$) was firstly dissolved into 25 mL mixed solvent composed of 10 mL of methanol and 15 mL of *N*,*N*-dimethyformamide (DMF) under mild stirring. Then, the above homogeneous solution was transferred into a 33 mL Teflon-lined stainless steel autoclave, sealed, and then heated to 180 ºC. After the autoclaves were maintained at 180 ºC for 24 h, the resulting product was centrifuged, rinsed with distilled water, and finally dried at 60 ºC in a vacuum.

Synthesis of the elongated assembly of rhombohedra: In a typical synthesis, 0.1 mmol of potassium permanganate ($KMnO_4$) was firstly dissolved into 25 mL mixed solvent composed of 5 mL of methanol and 20 mL of *N*,*N*-dimethyformamide (DMF) under mild stirring. Then, the above homogeneous solution was transferred into a 33 mL Teflon-lined stainless steel autoclave, sealed, and then heated to 180 ºC. After the autoclaves were maintained at 180 ºC for 24 h, the resulting product was centrifuged, rinsed with distilled water, and finally dried at 60 ºC in a vacuum.

Controlled Experiments: To elucidate the roles of different proportion of the mixed solvent in synthetic systems, controlled experiments were carried out. Irregular microblocks and microbipyramid were produced when the reactions were conducted in the pure CH_3OH and pure DMF, respectively. From the analysis of our above experiments, we believe that the $MnCO_3$ microcrystals are obtained with well defined morphologies and high quality crystalline due to the synergy of two different solvents. We speculate that it can form hydrogen bond between methanol and DMF (Figure S1), which could lead to slow oxidation of hydroxyl and aldehyde, so we can obtain monodispersed morphologies from the mixed solvent.

Characterization: The samples of as-prepared $MnCO_3$ nanostructures were characterized by X-ray powder diffraction (XRD) with Rigaku D/max Diffraction System using a Cu Kα source (λ = 0.15406 nm). The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL-2010 TEM at an acceleration voltage of 200 kV.

Table S1. Summary of the Experimental Parameters and Their Corresponding Morphologies of $MnCO_3$ Obtained under Different Conditions.

$KMnO_4$/g	CH_3OH/mL	DMF/mL	Morphology
0.158	25	0	irregular microblocks in Figure S2 a
0.158	10	15	steep rhombohedra in Figure 2
0.158	8	17	irregular rhombohedra in Figure 1B
0.158	5	20	the elongated assembly of rhombohedra in Figure 3
0.158	2	23	irregular elongated assembly in Figure 1B
0.158	0	25	Irregular elongated assembly of particles in Figure S2 b

All the reactions were conducted at 180 ºC for 24 h.

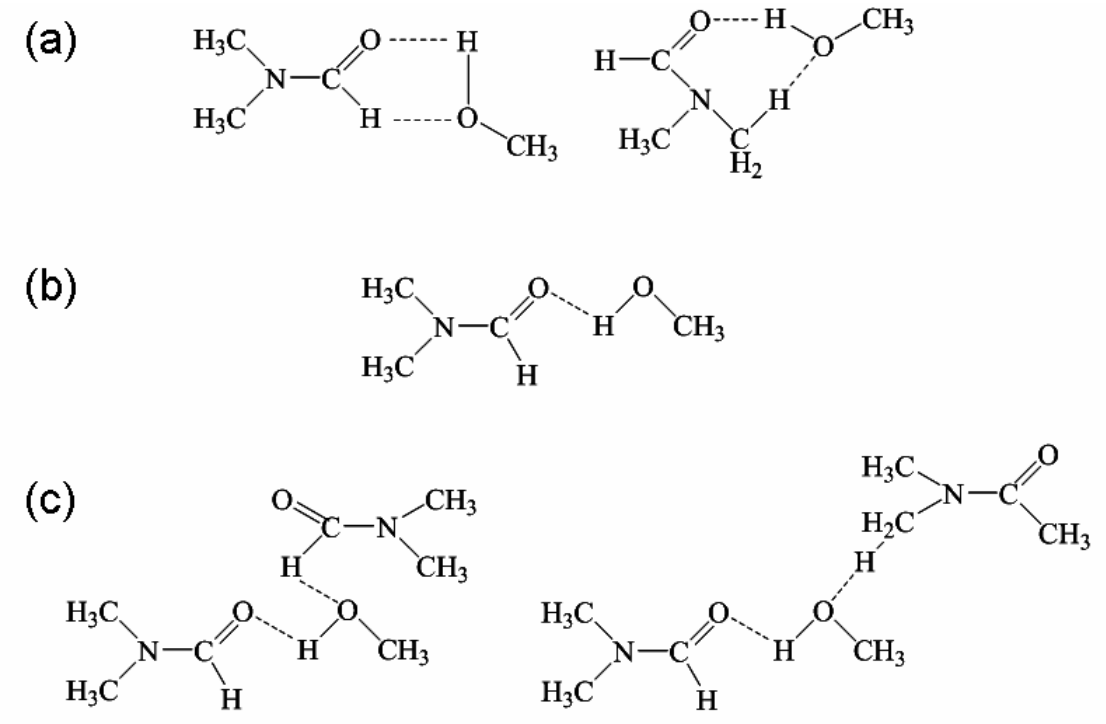

Figure S1. The schematic of hydrogen bond between methanol and DMF: (a) The preferred forms in the broad range of mixture compositions; (b) The preferred form in CH_3OH-rich mixtures; (c) The preferred forms in DMF-rich mixtures.[1]

[1] Stangret, J.; Kamieńska-Piotrowicz, E.; Szymańska-Cybulska, J. Analysis of Spectral Data by Complementary Methods: Inspection of The Molecular Complex in *N*,*N*-dimethylformamide–methanol Mixtures *Spectrochim. Acta, Part A* **2005,** *61,* 3043-3050.

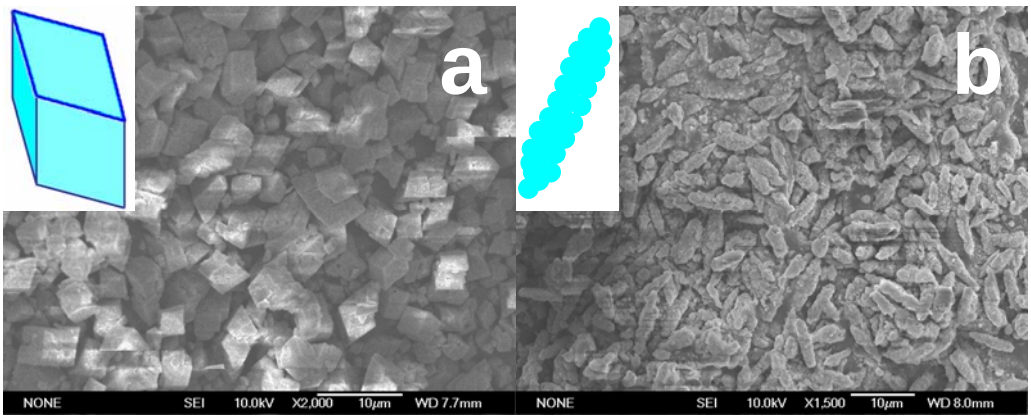

Figure S2. (a) SEM image of $MnCO_3$ microcrystals obtained from pure CH_3OH, the inset is the diagrammatic sketch of obtained crystal structure; (b) SEM image of $MnCO_3$ microcrystals obtained from pure DMF, the inset is the diagrammatic sketch of obtained crystal structure;

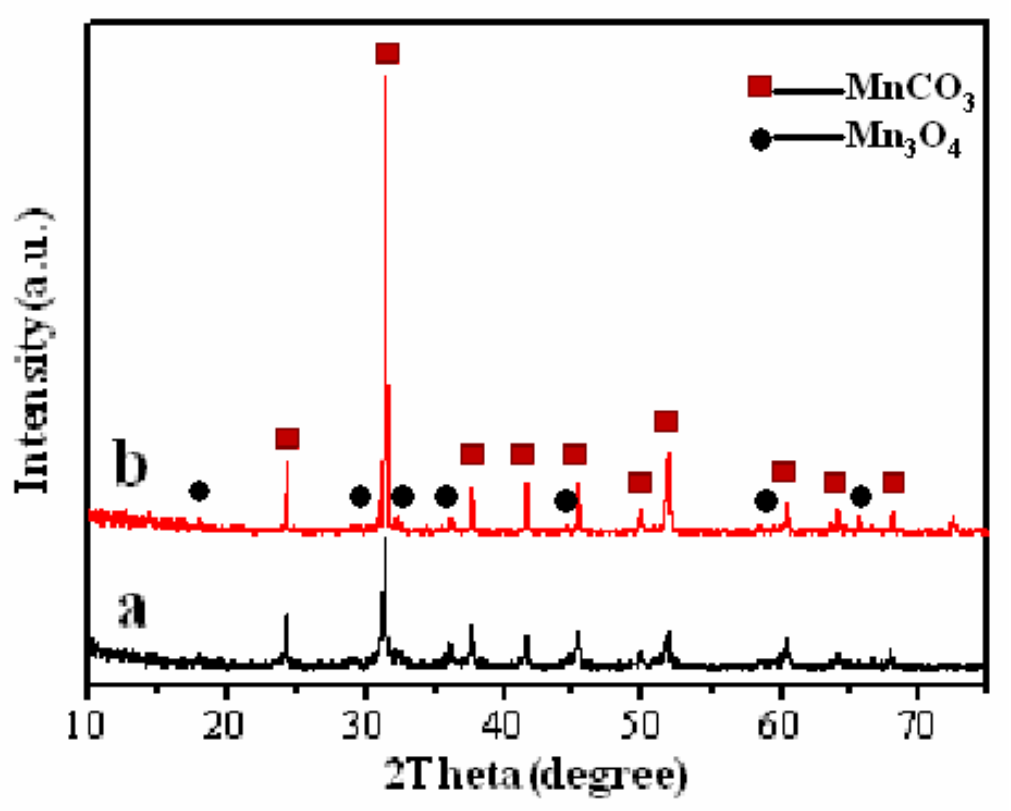

Figure S3. XRD patterns of as-synthesized samples from different solvent: (a) pure CH_3OH; (b) pure DMF.